

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 840 824 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
13.02.2002 Bulletin 2002/07

(51) Int Cl.7: **D21H 23/02**

(86) International application number:
PCT/US96/11780

(21) Application number: **96925330.1**

(87) International publication number:
WO 97/04171 (06.02.1997 Gazette 1997/07)

(22) Date of filing: **16.07.1996**

(54) **METHOD FOR MAKING SOFT TISSUE PAPER WITH IMPROVED BULK SOFTNESS AND SURFACE SOFTNESS**

VERFAHREN ZUR HERSTELLUNG WEICHEN TISSUE-PAPIERS MIT VERBESSERTER
BAUSCHWEICHKEIT UND OBERFLÄCHENWEICHKEIT

PROCEDE DE FABRICATION DE PAPIER TISSU AVEC UNE DOUCEUR EN VOLUME ET DE
SURFACE AMELIOREES

(84) Designated Contracting States:
BE DE ES FR GB IT NL SE

• **SMITH, Michael, John**
Neenah, WI 54956 (US)

(30) Priority: **21.07.1995 US 505838**

(74) Representative:
Diehl, Hermann, Dr. Dipl.-Phys. et al
DIEHL, GLÄSER, HILTL & PARTNER
Patentanwälte Augustenstrasse 46
80333 München (DE)

(43) Date of publication of application:
13.05.1998 Bulletin 1998/20

(56) References cited:
EP-A- 0 347 153 WO-A-94/05857
FR-A- 2 481 333 US-A- 3 755 220
US-A- 4 158 594 US-A- 4 447 294

(73) Proprietor: **KIMBERLY-CLARK WORLDWIDE, INC.**
Neenah, Wisconsin 54956 (US)

• **PATENT ABSTRACTS OF JAPAN vol. 013, no.**
308 (C-617), 14 July 1989 & JP,A,01 093506 (YUJI
KATO;OTHERS: 01), 12 April 1989,

(72) Inventors:
• **SCHROEDER, Wen, Zyo**
Appleton, WI 54914 (US)
• **ANDERSON, Gary, Vance**
Larsen, WI 54947 (US)
• **KRZYSIK, Duane, Gerard**
Appleton, WI 54911 (US)
• **SHANKLIN, Gary, Lee**
Appleton, WI 54915 (US)

Remarks:

The file contains technical information submitted
after the application was filed and not included in this
specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 840 824 B1

Description

[0001] Improving the softness of tissues is a continuing objective in tissue manufacture. In general, prior efforts have been directed at reducing the inter-fiber bonding within the tissue structure or coating the tissue surface with chemicals which improve the surface feel. Softness, however, is a perceived property of tissues comprising many factors including bulk, softness and surface smoothness. To date, efforts have tended to focus on one or the other. US-A-4,447,294 discloses a process for making soft, absorbent tissue paper webs. In the first step, according to US-A-4,447,294, a furnish of papermaking fibers and a wet strength resin is provided; a wet fibrous web is made from that furnish and the wet web is dried. In the next step, according to US-A-4,447,294, the wet strength resin in the web is at least partially cured. Finally, a nitrogenous cationic debonding agent is incorporated into the dried web according to US-A-4,447,294.

[0002] US-A-3,755,220 provides cellulosic sheet materials having an improved ratio of wet tensile strength to dry tensile strength which comprise cellulosic fibers; at least one debonder selected from the group consisting of anionic and cationic surface active agents; and a cationic thermosetting resin such as those normally employed to increase the wet strength of paper.

[0003] In EP-A-0,347,153 a process for making soft tissue paper is disclosed which includes the steps of wet-laying cellulosic fibers to form a web, applying to the wet web, at a fiber consistency level of from about 10% to about 80%, a polysiloxane material, and then drying and creping the web to form the finished tissue paper. The process according to EP-A-0,347,153 may further include the steps of applying an effective amount of a surfactant material to enhance softness and/or wettability control; and/or an effective amount of a binder material, such as a starch, for linting control, and/or to contribute tensile strength to the tissue paper.

[0004] WO-A-94/05857 describes a process for making soft tissue paper which includes providing a dry tissue web and then applying a sufficient amount of a chemical papermaking additive from a thin film to the dry web. The chemical papermaking additives according to WO-A-94/05857 are added to the surface of the tissue paper to enhance properties of the tissue such as strength, softener, absorbency and/or aesthetics.

[0005] Finally US-A-415 8594 discloses a method for forming a strong, soft, fibrous sheet material having substantial stretch in all directions in its own plane, by forming a web of cellulosic fibers having a basis weight of from about 9.5-104 g/m² (5 to about 55 pounds per ream of 2,880 square feet), adhering one surface of the web to a creping surface in a fine pattern arrangement by a bonding material adhered to one surface of the web and to the creping surface in the fine pattern arrangement, and creping the web from the creping surface to form the sheet material.

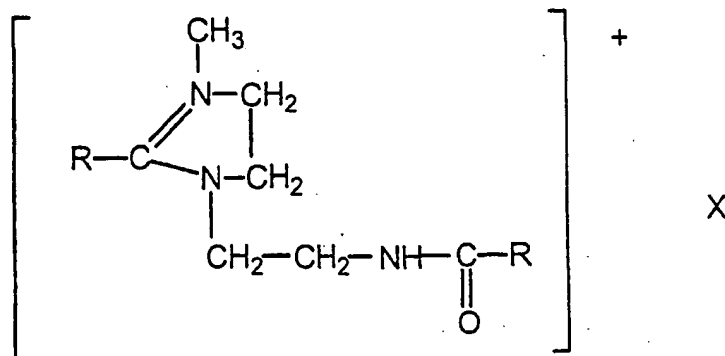
[0006] Hence, there is a need for a method which improved both bulk softness and surface softness.

Summary of the Invention

[0007] It has now been discovered that softness of tissues can be improved by the combined addition of one or more softener/debonders (hereinafter defined) to the tissue making furnish, followed by a second addition of one or more softener/debonders to the surface of the dried tissue. The initial introduction of the softener/debonder to the furnish provides more of a bulk softness to the tissue, while the subsequent topical application imparts a more smooth or slick surface feel. The combination results in a very soft-feeling tissue product.

[0008] More specifically, the invention resides in a method for making soft tissue comprising:

- (a) forming an aqueous suspension of papermaking fibers having from 0.01 to 6 weight percent, based on dry fiber, of a quaternary ammonium compound having the following structure:



wherein

X = chloride, methyl sulfate or other compatible counterion; and
R = aliphatic, saturated or unsaturated C₈-C₂₂;

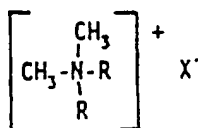
(b) forming a tissue web by depositing the aqueous suspension of papermaking fibers onto a forming fabric;

(c) dewatering and drying the tissue web; and

(d) topically applying to the dry tissue web from 0.01 to 10 weight percent, based on dry fiber, of one or more softener/debonders selected from the group consisting of quaternary ammonium compounds, quaternized protein compounds, phospholipids, silicone quaternaries, organoreactive polysiloxanes and silicone glycols. The softener/debinder which is topically applied to the dry web can be the same softener/debinder added to the furnish prior to forming the tissue web, or it can be different.

[0009] As used herein, "softener/debinder" is a chemical compound selected from the group consisting of quaternary ammonium compounds, quaternized protein compounds, phospholipids, silicone quaternaries, quaternized, hydrolyzed wheat protein/dimethicone phosphocopolyol copolymer, organoreactive polysiloxanes, and silicone glycols.

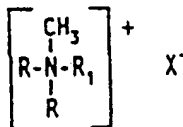
[0010] Suitable quaternary ammonium compounds have the following structures:



wherein

X = chloride, methyl sulfate, or other compatible counterion; and
R = aliphatic, saturated or unsaturated C₈ - C₂₂;

and



wherein

X = chloride, methyl sulfate, or other compatible counterion;

R = aliphatic, saturated or unsaturated C₈ - C₂₂; and

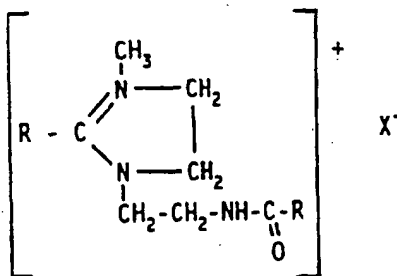
5 R₁ = benzyl or epoxy group;

and

10

15

20



wherein

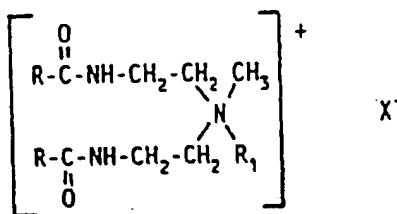
X = chloride, methyl sulfate, or other compatible counterion; and

25 R = aliphatic, saturated or unsaturated C₈-C₂₂;

and

30

35



40 wherein

X = methyl sulfate, chloride, or other compatible counterion;

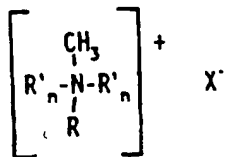
R = aliphatic, normal, saturated or unsaturated, C₈ - C₂₂; and

45

R₁ = 2-hydroxyethyl or 2-hydroxypropyl;

and

50



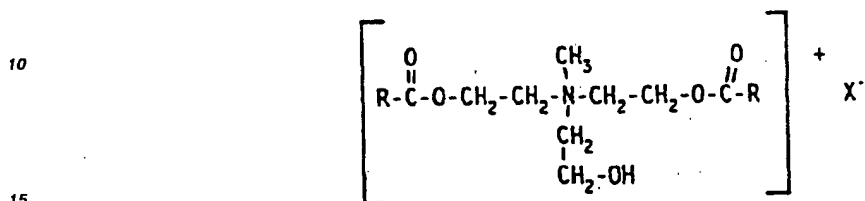
55

wherein

R = aliphatic, normal or branched, saturated or unsaturated, C₈ - C₂₂;

X = chloride, methyl sulfate, ethyl sulfate, or other compatible counterion;
 R' = 2-hydroxyethyl or polyethoxyethanol; and
 n = 1 to 50;

5 and

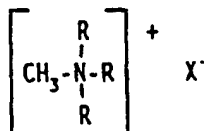


wherein

20 R = C₈ - C₂₂; and
 X = methyl sulfate, chloride, or other compatible counterion;

and

25



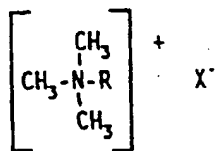
30

wherein

35 R = aliphatic alkyl, normal or branched, saturated or unsaturated, C₈ - C₂₂; and
 X = chloride, methyl sulfate or other compatible counterion.

and

40



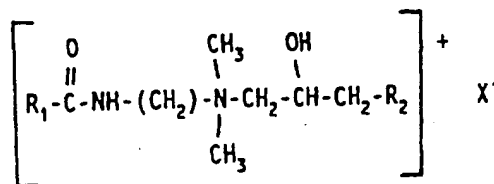
45

wherein

50 R = aliphatic, saturated or unsaturated, C₈ - C₂₂; or allyl-; or R'-O-CH₂-CH₂-CH₂, where R' = normal or branched,
 C₄ - C₁₈; and
 X = chloride, sulfate or any other compatible counterion.

[0011] Suitable quaternized protein compounds include the following structures:

55



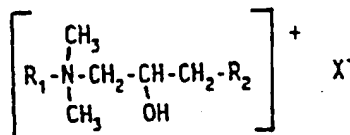
5

10 wherein

R_1 = fatty acid radical, saturated or unsaturated, $\text{C}_{12} - \text{C}_{22}$;
 R_2 = hydrolyzed soy protein, hydrolyzed silk protein, collagen, keratin moiety or hydrolyzed wheat protein; and
 X = chloride, lactate or other compatible counterion;

15

and



20

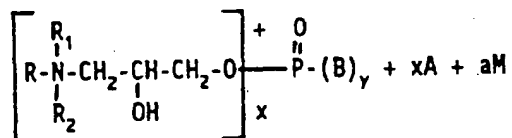
25

wherein

R_1 = fatty acid radical, saturated or unsaturated, $\text{C}_{12} - \text{C}_{22}$;
 R_2 = hydrolyzed collagen or keratin moiety; and
 X = chloride, lactate or other compatible counterion.

30

[0012] Suitable phospholipids include, without limitation, those having the following structures:



35

40

wherein

$x = 1$ to 3 ;

45

$x + y = 3$;

$a = 0$ to 2 ;

$\text{B} = \text{O}^-$ or OM ;

$\text{A} = \text{an anion}$;

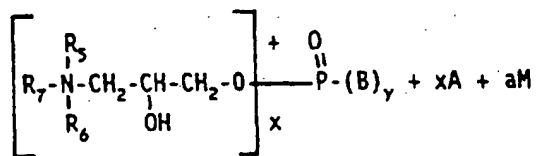
$\text{M} = \text{a cation}$; and

50

R , R_1 & R_2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 16 carbon atoms and the total carbon atoms of $\text{R} + \text{R}_1 + \text{R}_2 = 10$ to 24 ;

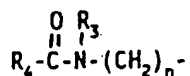
and

55



wherein

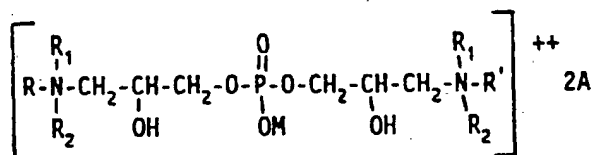
- $x = 1$ to 3 ;
 $x + y = 3$;
 $a = 0$ to 2 ;
 $B = O^-$ or OM ;
 $A =$ an anion;
 $M =$ a cation;
 R_5, R_6 may be the same or different, are alkyl, hydroxyalkyl, carboxyalkyl of up to C_6 , or polyoxyalkylene of up to C_{10} ; or R_5, R_6 and the nitrogen they are attached to may represent an N-heterocycle; and
 $R_7 =$ an amidoamine moiety of the formula:



wherein

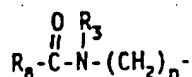
- $n = 2$ to 6 ;
 $R_3 =$ hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons; or cycloalkyl of up to 6 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms; and
 $R_4 =$ alkyl, alkenyl, alkoxy or hydroxyalkyl, C_5-C_{21} , or aryl or alkaryl of up to C_{20} ;

and



wherein

- $A =$ an anion;
 $M =$ a cation;
 R, R_1 & R_2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 16 carbon atoms, and the total carbon atoms of $R + R_1 + R_2 = 10$ to 24 ; and
 R' is an amidoamine moiety of the structure:

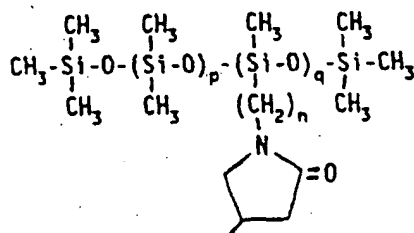


wherein

$n = 2$ to 6 ;

R_3 = hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons; or cycloalkyl of up to 6 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms; and

R_8 has the following structure:



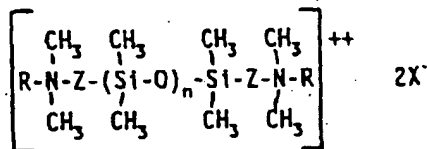
wherein

$n = 3$ or greater;

$p = 1$ to 1000 ;

$q = 1$ to 25 .

[0013] Suitable silicone quaternaries include the following structure:



wherein

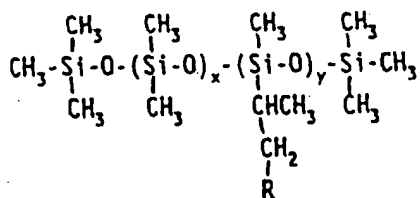
R = alkyl group, $C_{12} - C_{18}$;

Z = $-\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} - (\text{CH}_2)_3 -$;

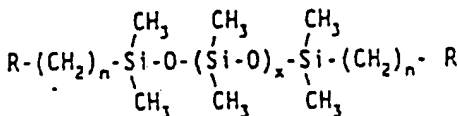
X = alkoxy, chloride or other compatible counterion; and

$n = 1$ to 50 .

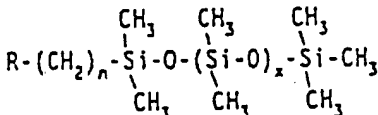
[0014] Suitable organoreactive polysiloxanes include the following structures:



and



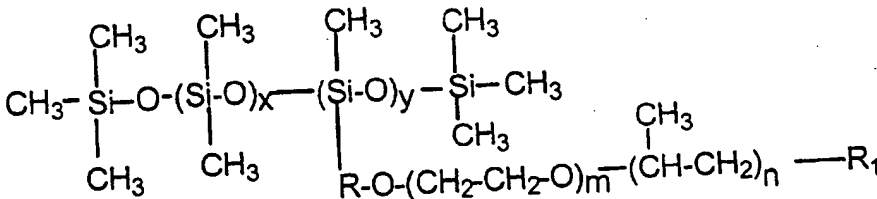
and



wherein

R = amine, carboxy, hydroxy, or epoxy;
n = 3 or greater;
x = 1 to 1000; and
y = 1 to 25.

[0015] Suitable silicone glycols include the following structure:



wherein

R = alkyl group, C₁-C₆;
R₁ = acetate or hydroxy group;
x = 1 to 1000;
y = 1 to 50;
m = 1 to 30; and
n = 1 to 30.

[0016] When a combination of softener/debonder is desired, the combination can be added to the thick stock simultaneously or separately. The combinations can contain one or more compounds from the above groups and added to the slurry, either in a premixed form or individually metered.

[0017] The final tissue sheet comprises from about 0.01 to about 6 percent (by weight of the fiber) of the softener/debonders added to the wet end of the tissue making process, individually or in combination. More preferably, the final tissue sheet comprises from about 0.1 to about 3 percent of the softener/debinder added at the wet end, based on the weight of the fiber.

[0018] Softener/debonders used for the topical treatment can be delivered in an aqueous solution or be dissolved in a suitable solvent such as propylene glycol, ethylene glycol, polyethylene glycol, isopropyl alcohol, methanol, ethanol or other organic solvents. They can be applied to the surface of the basesheet individually or in combination with others. It is preferred that the composition for topical treatment comprises from about 1 to about 100 weight percent of the softener/debinder (individually or in combination), more preferably from about 35 to about 80 weight percent. It is also preferred that the softener/debinder be topically added to the tissue sheet at an add-on ratio of from about 0.01 to

about 10 weight percent of the fiber, and more preferably from about 0.1 to about 2 weight percent of the fiber.

[0019] Suitable methods for the topical treatment include, but are not limited to spraying, rotogravure printing, trailing blade coating, flexographic printing, and the like.

5 Examples

Example 1

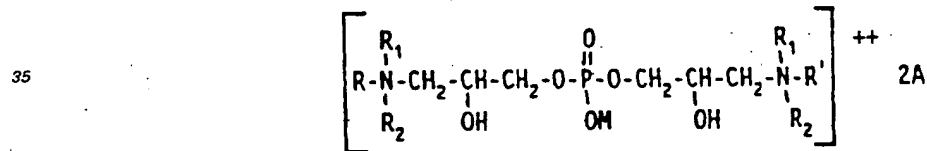
[0020] A 2-ply, wet-pressed, creped tissue was made using a layered headbox. The first stock layer (the layer which ultimately contacts the Yankee dryer surface) contained eucalyptus hardwood fiber and provided 60 dry weight percent of the tissue sheet. The remaining 40 percent of the tissue sheet was provided via a second stock layer consisting of northern softwood kraft pulp. The total basis weight of the sheet was 13,6 g/m² (7.3 pounds per 2880 square feet) of air dried tissue. Two strength agents were added to the fiber stock layers prior to the headbox. Parex 631NC (a gly-oxalated polyacrylamide from Cytec Industries, Inc.) was metered into the softwood thick stock at 0.08 to 0.1 percent of the total fiber weight. Another strength agent, Kymene 557 LX (commercially available from Hercules, Inc.) was metered into both the hardwood and the softwood thick stock at 0.05 and 0.1 percent of the total fiber weight, respectively.

[0021] A quaternary ammonium compound softener/debinder (methyl-1-oleyl amidoethyl-2-oleyl imidazolium methyl sulfate identified as Varisoft 3690 available from Witco Corporation, 90 percent active matter) was added to the hardwood thick stock at 0.17 percent of the total fiber weight.

[0022] After drying and creping, the tissue sheet was plied together with a like sheet to form a two-ply tissue. The hardwood layer of both plies was rotogravure-printed with a 40 percent emulsion of an organoreactive polysiloxane (FTS-226 made by OSI Specialties, Inc.) at an add-on amount of 1 percent per ply based on the weight of fiber. The resulting tissue product had increased bulk with improved surface smoothness.

Example 2

[0023] A 2-ply layered tissue was made as described in Example 1, except instead of rotogravure-printing both plies with an organoreactive polysiloxane, both plies were instead coated with a silicone phospholipid (Mona Industries, Inc., Item Code #54146, Lot 2426, 25-30% active) having the following structure:



wherein

A = chloride ion;

M = sodium ion;

R₁ = R₂ = -CH₃

R can be alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 16 carbon atoms, and the total carbon atoms of R + R₁ + R₂ = 10 to 24; and

R' is an amidoamine moiety of the structure:

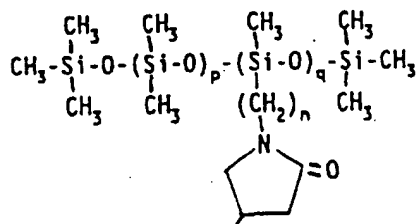


wherein

n = 3;

R₃ = hydrogen; and

R₈ has the following structure:



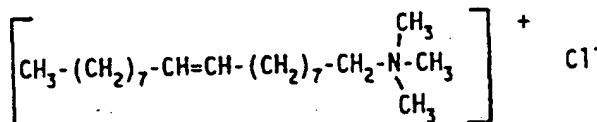
wherein

$$\begin{array}{l}
 n = 3; \\
 p = 90; \\
 q = 1.
 \end{array}$$

[0024] A trailing blade coater was used to apply the silicone phospholipid. The blade angle was set at 30° and blade pressures were varied between 20 and 40 psi to deliver different levels of addition. The resulting tissue products had increased bulk and smooth surface feel.

Example 3

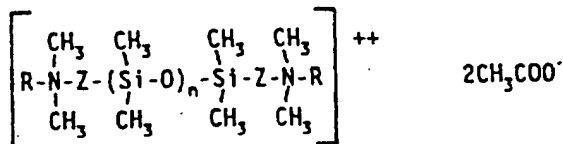
[0025] A 2-ply tissue was made as described in Example 2, except both plies were coated with a quaternary ammonium compound (olealkonium chloride, Mackernium KP made by McIntyre Group, LTD., 50% active) having the following structure:



[0026] The resulting tissue products had increased bulk and smooth surface feel.

Example 4

[0027] A 2-ply layered tissue was made as described in Example 2, except both plies were coated with a silicone quaternary compound (Ablquat 3272 made by Goldschmidt Chemical Corporation, 50% active) having the following structure:



wherein

$$\begin{array}{l}
 \text{R} = \text{alkyl group, } \text{C}_{12} - \text{C}_{18}; \\
 \text{Z} = -\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} - (\text{CH}_2)_3 -; \text{ and} \\
 n = 1 \text{ to } 50.
 \end{array}$$

[0028] The resulting tissue products had increased bulk and smooth surface feel.

Example 5

[0029] A 2-ply layered basesheet was made as described in Example 2, except both plies were printed with an aqueous composition comprising 50% of organopolydimethylsiloxane (FTS-226) and 50% quaternary ammonium compound (Mackernium KP). The resulting tissue products had increased bulk and smooth surface feel.

Example 6

[0030] A 2-ply layered basesheet was made as described in Example 1, except both plies were coated with an aqueous composition comprising 40% quaternary ammonium compound (Mackernium NLE made by McIntyre Group, LTD.), 40% organopolydimethylsiloxane (FTS-226) and 20% water. Mackernium NLE is an alkylamidopropyl epoxy-propyl diammonium chloride, 100 percent active.

[0031] The resulting tissue products had increased bulk and smooth surface feel.

Example 7

[0032] A two-ply layered basesheet was made as described in Example 2, except both plies were coated with an aqueous composition comprising 25% quaternary ammonium compound (Mackernium KP), 25% organopolysiloxane (FTS-226) and 50% propylene glycol. The resulting tissue products had increased bulk and smooth surface feel.

Example 8

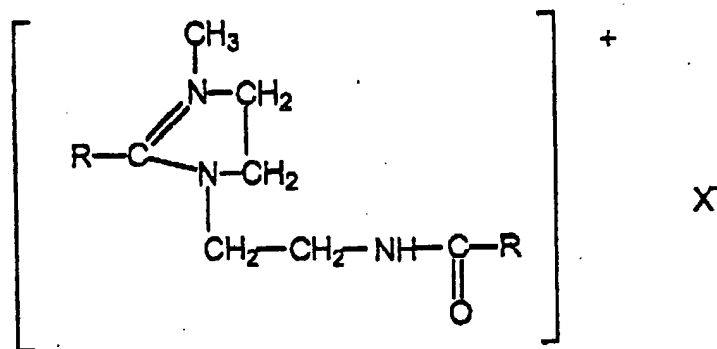
[0033] A one-ply, uncreped, through-air-dried tissue was made using a layered headbox. The two outer layers contained bleached eucalyptus hardwood kraft pulp processed through a Maule shaft disperser with a power input of 80 kilowatts at a consistency of about 34 percent and at a temperature of 84.4°C (184°F). The two outer layers made up 70 percent of the tissue sheet by weight of fiber. The middle layer constituted the remaining 30 percent of the tissue web and consisted of bleached northern softwood kraft pulp. The total basis weight of the sheet was 33.9 grams per square meter of air-dried tissue. The inner layer was refined to obtain sufficient dry strength in the final product. A wet strength agent (Parez 631NC) was metered into the inner layer at a rate of 5 kilograms per tonne or 0.5 percent of the weight of fiber. A softener/debonder (quaternary imidazolinium, fatty acid alkoxylate and polyether with 200 - 800 molecular weight, identified as DPSC 5299-8 from Witco Corporation) was added to the two outer layers at a rate of 5.25 kilograms per tonne (0.525 percent) of the total fiber weight. The thick stock of all layers was diluted to approximately 0.12 percent consistency prior to forming, dewatering and drying the tissue web.

[0034] After drying, the tissue was coated with a silicone diquaternary compound (Abilquat 3272) similar to Example 4. The resulting tissue product had a smoother surface feel compared to the tissue without coating.

Claims

1. A method for making a soft tissue comprising:

(a) forming an aqueous suspension of papermaking fibers having from 0.01 to 6 weight percent, based on dry fiber, of a quaternary ammonium compound having the following structure:



wherein

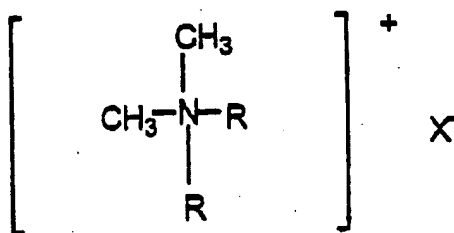
X = chloride, methyl sulfate or other compatible counterion; and
R = aliphatic, saturated or unsaturated C₈-C₂₂;

(b) forming a tissue web by depositing the aqueous suspension of papermaking fibers onto a forming fabric;

(c) dewatering and drying the tissue web; and

(d) topically applying to the dry tissue web from 0.01 to 10 weight percent, based on dry fiber, of one or more softener/debonders selected from the group consisting of quaternary ammonium compounds, quaternized protein compounds, phospholipids, silicone quaternaries, organoreactive polysiloxanes, and silicone glycols.

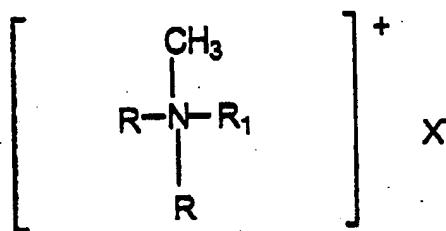
2. The method of Claim 1 wherein the amount of softener/debinder added to the fiber suspension is from 0.1 to 3 dry weight percent based on the amount of fiber.
3. The method of Claim 1 wherein the amount of softener/debinder topically applied to the dried web is from 0.1 to 10 dry weight percent, based on the amount of fiber.
4. The method of Claim 1 wherein at least one of the softener/debinders in step d) is a quaternary ammonium compound having the following structure:



wherein

X = chloride, methyl sulfate, or other compatible counterion; and
R = aliphatic, saturated or unsaturated C₈-C₂₂.

5. The method of Claim 1 wherein at least one of the softener/debinders in step d) is a quaternary ammonium compound having the following structure:



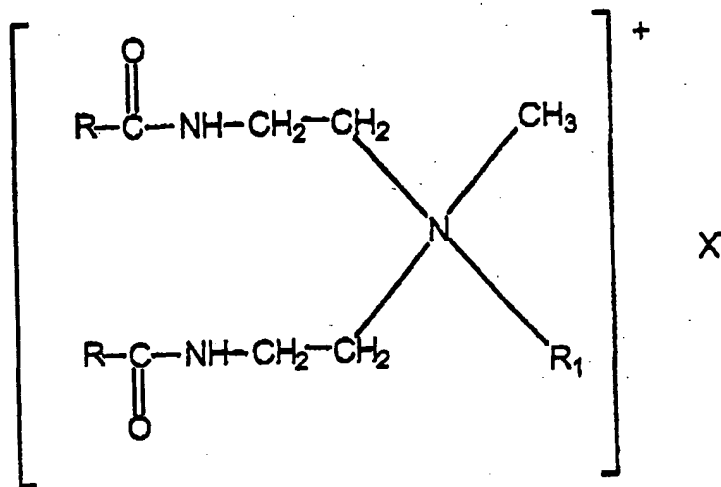
wherein

X = chloride, methyl sulfate, or other compatible counterion;

R = aliphatic, saturated or unsaturated C₈-C₂₂;

R_1 = benzyl or epoxy group,

6. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a quaternary ammonium compound having the following structure:



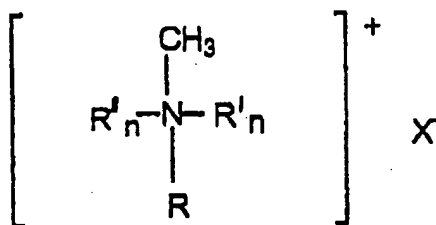
wherein

X = methyl sulfate, chloride, or other compatible counterion;

R = aliphatic, normal saturated or unsaturated, C₈-C₂₂

R₁ = 2-hydroxyethyl or 2-hydroxypropyl;

7. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a quaternary ammonium compound having the following structure:



wherein

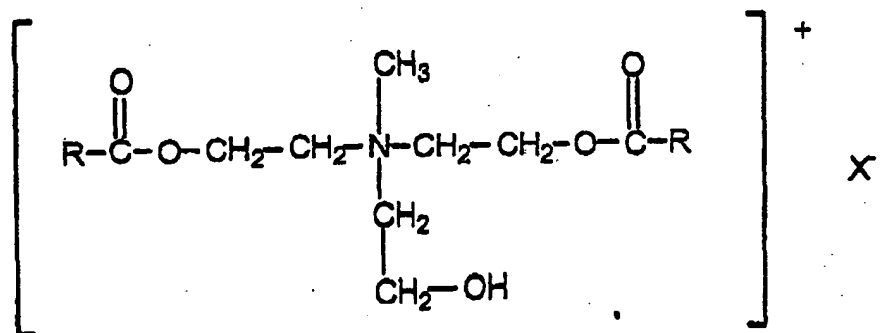
R = aliphatic, normal or branched, saturated or unsaturated C₈-C₂₂;

X = chloride, methyl sulfate, ethyl sulfate, or other compatible counterion;

R' = 2-hydroxyethyl or polyethoxyethanol; and

n = 1 to 50.

8. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a quaternary ammonium compound having the following structure:

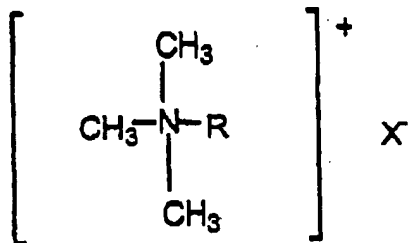


wherein

R = C₈-C₂₂; and

X = methyl sulfate, chloride, or other compatible counterion.

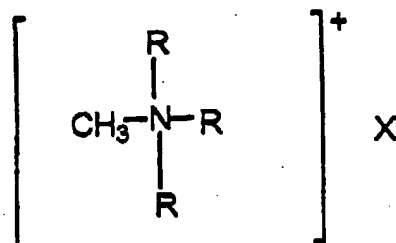
9. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a quaternary ammonium compound having the following structure:



wherein

R = aliphatic, saturated or unsaturated C₈-C₂₂; or allyl-; or R'-O-CH₂-CH₂-CH₂, where R' = normal or branched, C₄-C₁₈; and
 X = chloride, sulfate or any other compatible counterion.

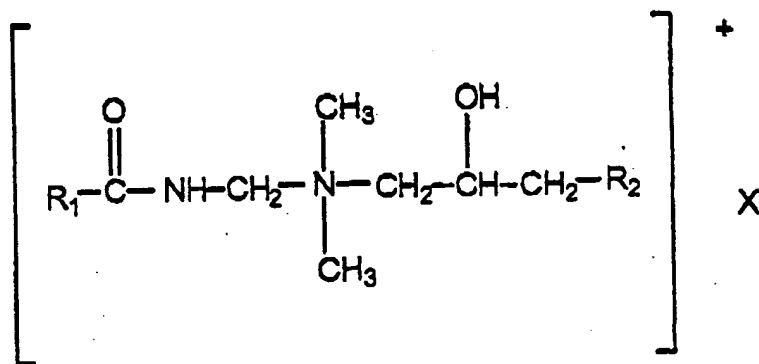
10. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a quaternary ammonium compound having the following structure:



wherein

R = aliphatic alkyl, normal or branched, saturated or unsaturated C₈-C₂₂; and
 X = chloride, methyl sulfate, or other compatible counterion.

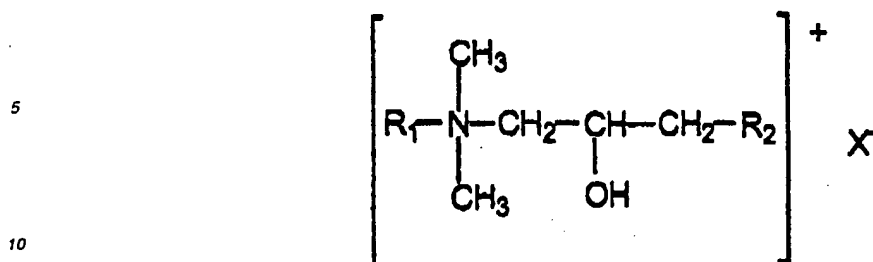
11. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a quaternized protein compound having the following structure:



wherein

R₁ = fatty acid radical, saturated or unsaturated, C₁₂-C₂₂;
 R₂ = hydrolyzed soy protein, hydrolyzed silk protein, hydrolyzed wheat protein, collagen moiety, or keratin moiety; and
 X = chloride, lactate, or other compatible counterion.

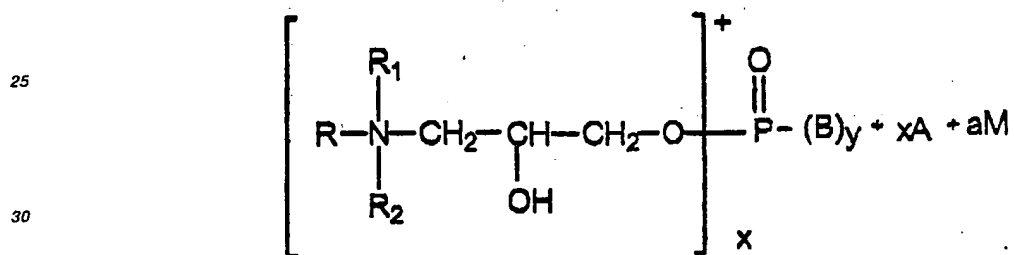
12. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a quaternized protein compound having the following structure:



wherein

- 15 R_1 = fatty acid radical, saturated or unsaturated, C_{12} - C_{22} ;
 R_2 = hydrolyzed collagen or keratin moiety; and
 X = chloride, lactate, or other compatible counterion.

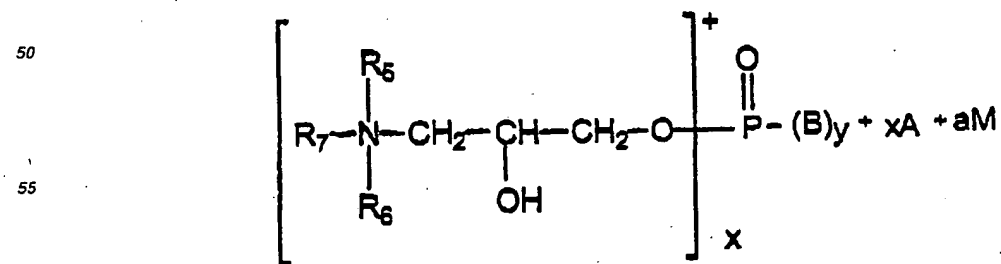
- 20 13. The method of claim 1 wherein at least one of the softener/debonders in step is a phospholipid having the following structure:



wherein

- 35 $x = 1$ to 3 ;
 $x + y = 3$;
 $a = 0$ to 2 ;
 $\text{B} = \text{O}^-$ or OM
 $\text{A} = \text{an anion}$
 $\text{M} = \text{a cation}$; and
 R , R_1 & R_2 can be the same or different, are alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 16 carbon atoms and the total carbon atoms of $\text{R} + \text{R}_1 + \text{R}_2 = 10$ to 24 .

- 45 14. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a phospholipid having the following structure:



wherein

x = 1 to 3;

x + y = 3;

a = 0 to 2;

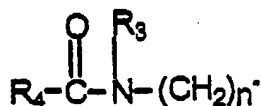
B = O⁻ or OM;

A = an anion;

M = a cation;

R₅, R₆ may be the same or different, are alkyl, hydroxyalkyl, carboxyalkyl of up to C₆, or polyoxyalkylene of up to C₁₀; or R₅, R₆ and the nitrogen they are attached to may represent an N-heterocycle; and

R₇ = an amidoamine moiety of the formula;



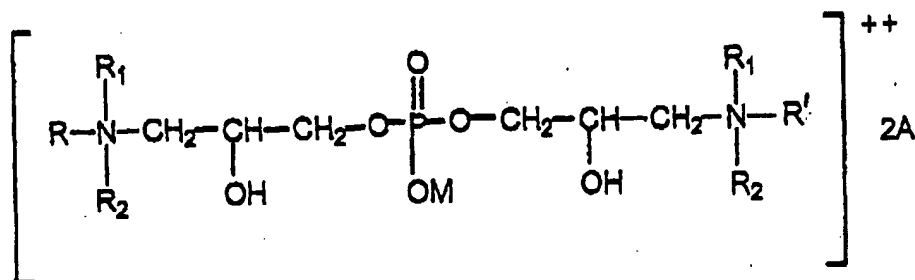
wherein

n = 2 to 6;

R₃ = hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbons; or cycloalkyl of up to 6 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms; and

R₄ = alkyl, alkenyl, alkoxy or hydroxyalkyl, C₅-C₂₁, or aryl or alkaryl of up to C₂₀.

15. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a phospholipid having the following structure:



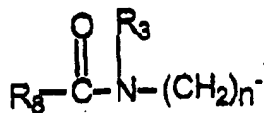
wherein

A = anion;

M = a cation;

R, R₁ & R₂ can be the same or different, are alkyl, substituted alkyl, alkyl aryl or alkenyl groups of up to 16 carbon atoms, and the total carbon atoms of R + R₁ + R₂ = 10 to 24; and

R' is an amidoamine moiety of the structure:

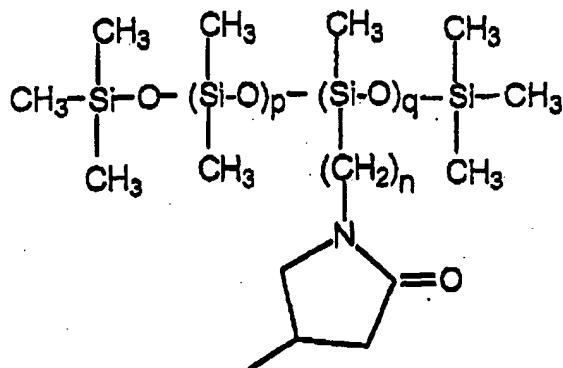


wherein

$n = 2$ to 6 ;

R_3 = hydrogen or alkyl, hydroxalkyl or alkenyl of up to 6 carbons; or cycloalkyl of up to 6 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms; and

R_8 has the following structure:



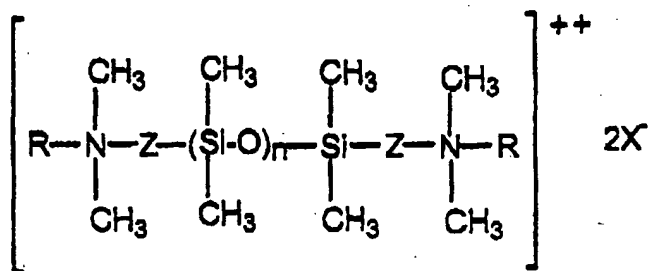
wherein

$n = 3$ or greater

$p = 1$ to 1000 ; and

$q = 1$ to 25 .

16. The method of Claim 1 wherein at least one of the softener/debonders in step d) is a silicone quaternary having the following structure:



wherein

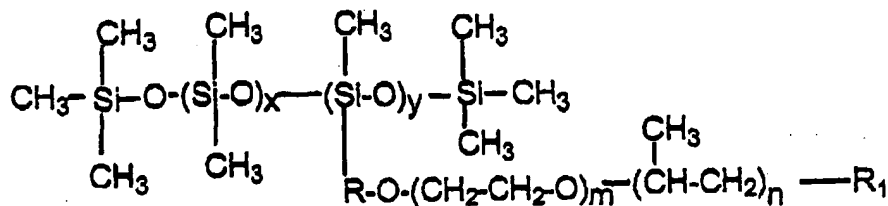
R = alkyl group, C_{12} - C_{18} ;

Z = $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-(\text{CH}_2)_3-$;

X = alkoxy, chloride or other compatible counterion; and

$n = 1$ to 50 .

17. The method of Claim 1 wherein at least one of the softener/debinder in step d) is a silicone having the following formula:



wherein

R=alkylen, C₁-C₈:

R1=acetate or hydroxyl group;

x=1 to 1000

y=1 to 50

m=1 to 30; and

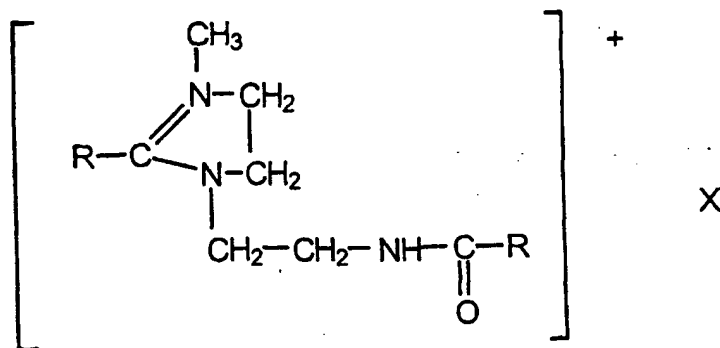
$n=1$ to 30.

18. The method of Claim 1 wherein at least one of the softeners/debonders in step d) is a quaternized, hydrolyzed wheat protein/dimethicone phosphocopolyol copolymer.
19. The method of Claim 1 wherein the softener/debinder added to the dried web is carried by a solvent selected from the group consisting of water, propylene glycol, ethylene glycol, polyethylene glycol, isopropyl alcohol, methanol and ethanol.

Patentansprüche

- 1. Verfahren zur Herstellung eines weichen Tissues, umfassend:**

(a) Bilden einer wässrigen Suspension aus Fasern zur Papierherstellung, die zwischen 0,01 und 6 Gewichtsprozent, basierend auf Trockenfasern, einer quartären Ammoniumverbindung umfassen, mit der folgenden Struktur:



wobei

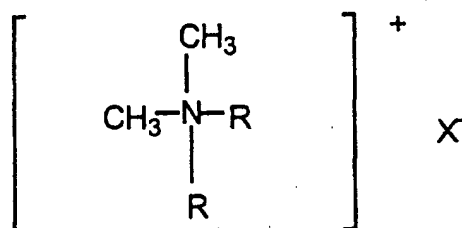
X = Chlorid, Methylsulfat oder anderes kompatibles Gegenion; und
R = aliphatische, gesättigte oder ungesättigte C₈-C₂₂;

(b) Bilden einer Tissuebahn durch Ablagern der wässrigen Suspension aus Fasern zur Papierherstellung auf einem Formbildungstoff;

(c) Entwässern und Trocknen der Tissuebahn; und

(d) örtliches Aufbringen auf der trockenen Tissuebahn von 0,01 bis 10 Gewichtsprozent, basierend auf den Trockenfasern, einer oder mehrerer Weichmacher/Bindungslöser, ausgewählt aus der Gruppe bestehend aus quartären Ammoniumverbindungen, quaternisierten Proteinverbindungen, Phospholipiden, Silikon-Quaternären, organoreaktiven Polysiloxanen und Silikonglykolen.

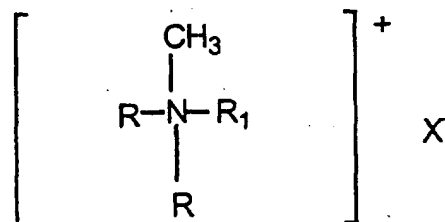
2. Verfahren gemäß Anspruch 1, wobei die Menge an der Fasersuspension zugefügtem Weichmacher/Bindungslöser zwischen 0,01 und 3 Trockengewichtsprozent liegt, basierend auf der Menge an Fasern.
3. Verfahren gemäß Anspruch 1, wobei die Menge an örtlich auf der getrockneten Bahn aufgebrachtem Weichmacher/Bindungslöser zwischen 0,1 und 10 Trockengewichtsprozent liegt, basierend auf der Menge an Fasern.
4. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quartäre Ammoniumverbindung ist, mit der folgenden Struktur:



wobei

X = Chlorid, Methylsulfat oder anderes kompatibles Gegenion; und
R = aliphatische, gesättigte oder ungesättigte C₈-C₂₂.

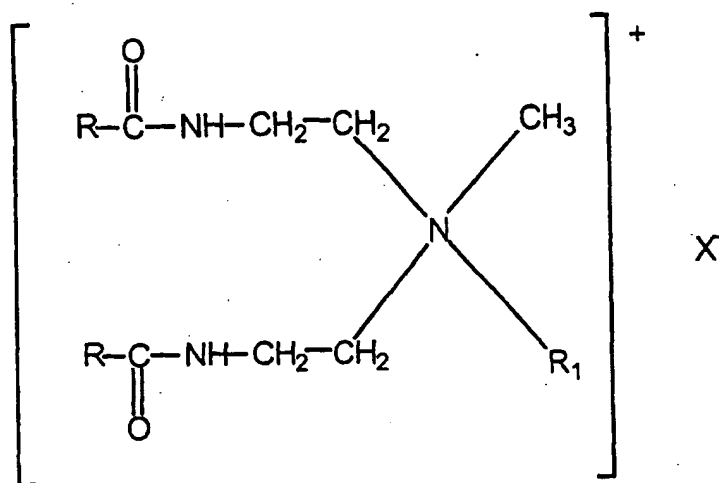
5. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quartäre Ammoniumverbindung mit der folgenden Struktur ist:



wobei

X = Chlorid, Methylsulfat oder anderes kompatibles Gegenion;
R = aliphatische, gesättigte oder ungesättigte C₈-C₂₂;
R₁ = Benzyl- oder Epoxygruppe.

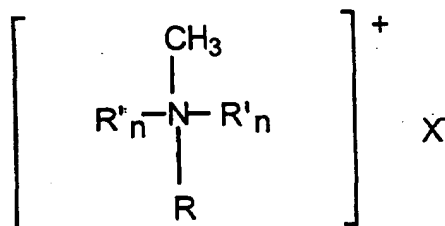
6. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quartäre Ammoniumverbindung mit der folgenden Struktur ist:



wobei

- X = Methylsulfat, Chlorid oder anderes kompatibles Gegenion;
 R = aliphatisch, normal gesättigt oder ungesättigt, C₈-C₂₂;
 R₁ = 2-Hydroxyethyl oder 2-Hydroxypropyl;

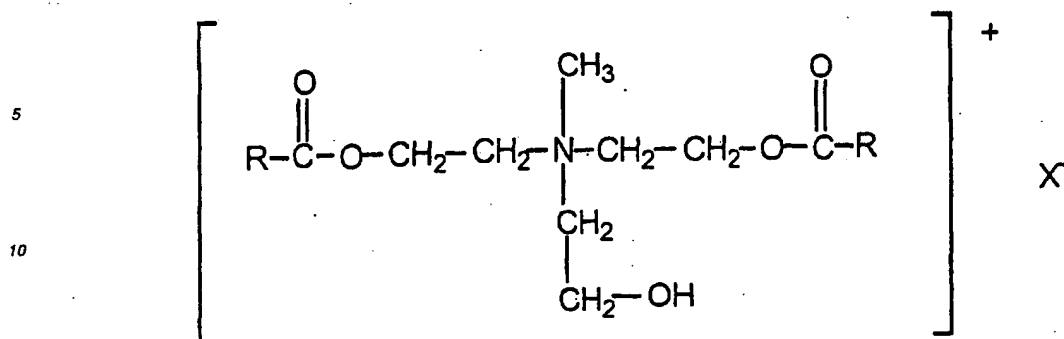
7. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quartäre Ammoniumverbindung mit der folgenden Struktur ist:



wobei

- R = Aliphatisch, normal oder verzweigt, gesättigt oder ungesättigt C₈-C₂₂;
 X = Chlorid, Methylsulfat, Ethylsulfat oder anderes kompatibles Gegenion;
 R' = 2-Hydroxyethyl oder Polyethoxyethanol; und
 n = 1 bis 50.

8. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quartäre Ammoniumverbindung mit der folgenden Struktur ist:

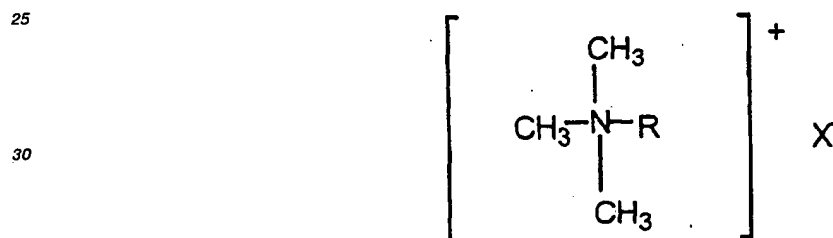


wobei

R = C₈-C₂₂; und

X = Methylsulfat, Chlorid oder anderes kompatibles Gegenion.

9. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quartäre Ammoniumverbindung mit der folgenden Struktur ist:

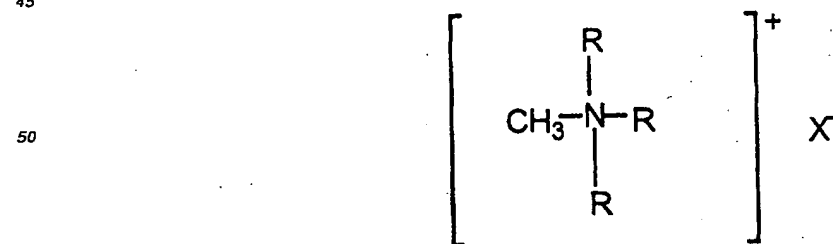


wobei

R = aliphatisch, gesättigtes oder ungesättigtes C₈-C₂₂; oder Allyl-; oder R'-O-CH₂-CH₂-CH₂, wobei R' = normal oder verzweigt, C₄-C₁₈; und

X = Chlorid, Sulfat oder irgendein anderes kompatibles Gegenion.

10. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quartäre Ammoniumverbindung mit der folgenden Struktur ist:

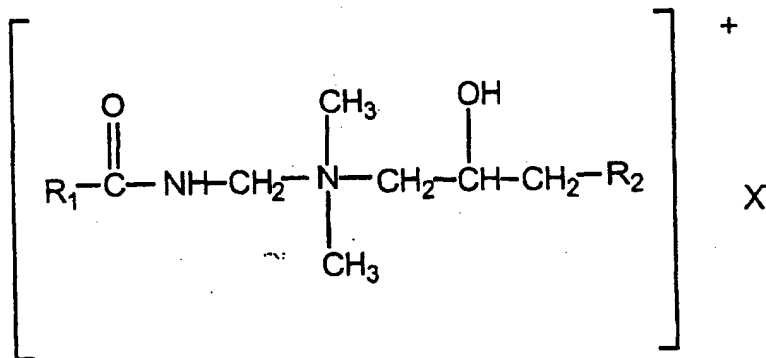


wobei

R = aliphatisches Alkyl, normal oder verzweigt, gesättigt oder ungesättigt C₈-C₂₂; und

X = Chlorid, Methylsulfat oder anderes kompatibles Gegenion.

11. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quarter-nisierte Proteinverbindung mit der folgenden Struktur ist:



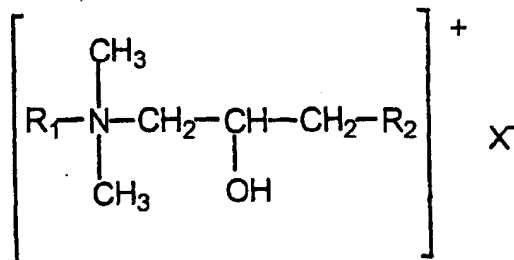
wobei

R₁ = Fettsäureradikal, gesättigt oder ungesättigt, C₁₂ - C₂₂;

R₂ = Hydrolisiertes Sojaprotein, hydrolisiertes Seidenprotein, hydrolisiertes Weizenprotein, Kollageneinheit oder Keratineinheit; und

X = Chlorid, Laktat oder anderes kompatibles Gegenion.

12. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) eine quarter-nisierte Proteinverbindung mit der folgenden Struktur ist:



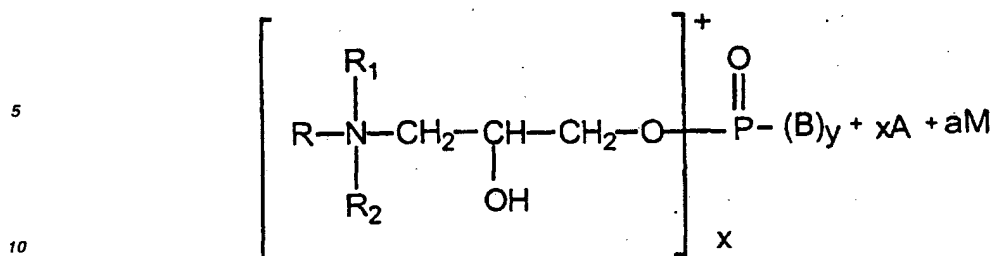
wobei

R₁ = Fettsäureradikal, gesättigt oder ungesättigt, C₁₂ - C₂₂;

R₂ = hydrolisierte Kollagen- oder Keratineinheit; und

X = Chlorid, Laktat oder anderes kompatibles Gegenion.

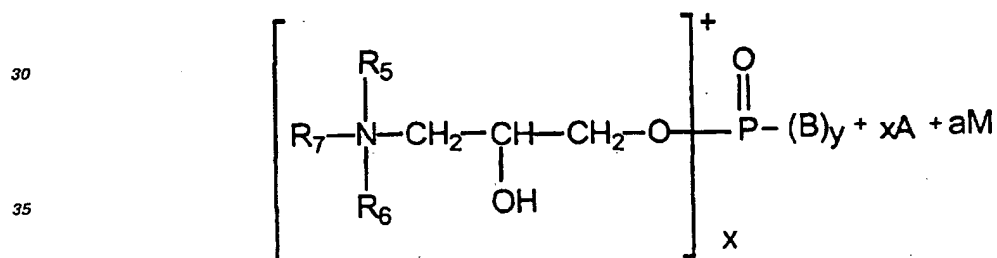
13. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) ein Phospholipid mit der folgenden Struktur ist:



wobei

- $x = 1$ bis 3 ;
 $x + y = 3$;
 $a = 0$ bis 2 ;
 $B = O^-$ oder OM ;
 $A =$ ein Anion;
 $M =$ ein Kation; und
 R, R_1 & R_2 können gleich oder verschieden sein, sind Alkyl-, substituierte Alkyl-, Alkylaryl- oder Alkenylgruppen mit bis zu 16 Kohlenstoffatomen und die gesamten Kohlenstoffatome von $R + R_1 + R_2 = 10$ bis 24 .

14. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) ein Phospholipid mit der folgenden Struktur ist:



wobei

- $x = 1$ bis 3 ;
 $x + y = 3$;
 $a = 0$ bis 2 ;
 $B = O^-$ oder OM ;
 $A =$ ein Anion;
 $M =$ ein Kation;
 R_5, R_6 können gleich oder verschieden sein, sind Alkyl, Hydroxyalkyl, Carboxyalkyl mit bis zu C_6 oder Polyoxyalkylen mit bis zu C_{10} ; oder
 R_5, R_6 und der Stickstoff, an den sie gebunden sind, können einen N-Heterocyclen bilden; und
 $R_7 =$ eine Amidoamineinheit der Formel:



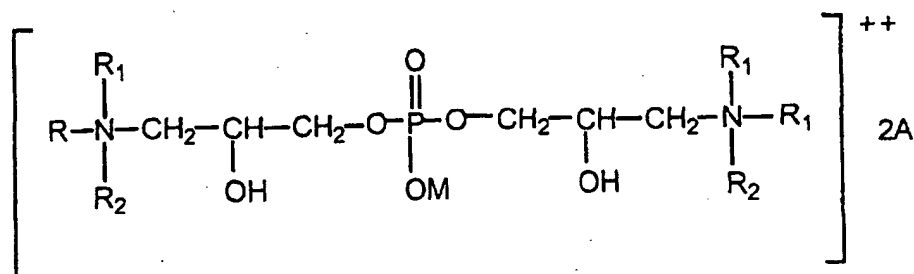
wobei

$n = 2$ bis 6

$R_3 =$ Wasserstoff oder Alkyl, Hydroxyalkyl oder Alkenyl mit bis zu 6 Kohlenstoffen; oder Cycloalkyl mit bis zu 6 Kohlenstoffatomen, oder Polyoxyalkylen mit bis zu 10 Kohlenstoffatomen; und

$R_4 =$ Alkyl, Alkenyl, Alkoxy oder Hydroxyalkyl, $C_5 - C_{21}$, oder Aryl oder Alkaryl mit bis zu C_{20} .

15. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) ein Phospholipid mit der folgenden Struktur ist:



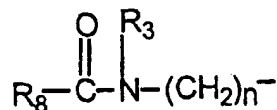
wobei

A = ein Anion;

M = ein Kation;

R, R_1 & R_2 können gleich oder verschieden sein, sind Alkyl-, substituierte Alkyl-, Alkylaryl- oder Alkenylgruppen mit bis zu 16 Kohlenstoffatomen und die gesamten Kohlenstoffatome von $R + R_1 + R_2 = 10$ bis 24 ; und

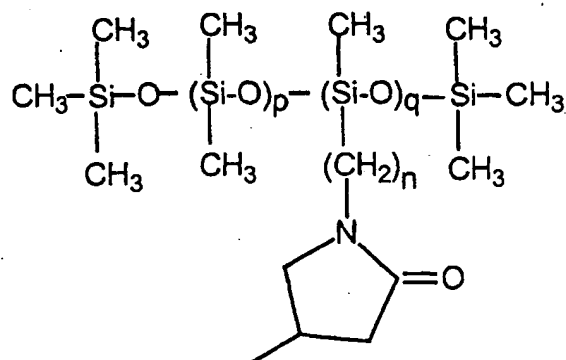
R' ist eine Amidoamineinheit mit der Formel:



wobei

$n = 2$ bis 6 ;

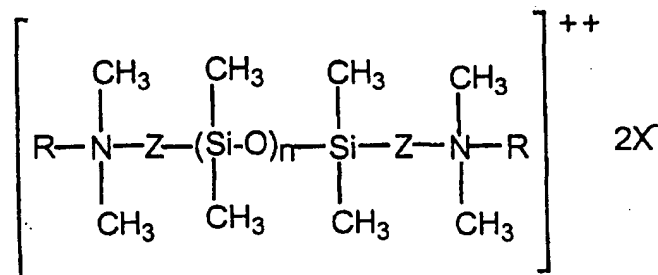
$R_3 =$ Wasserstoff oder Alkyl, Hydroxyalkyl oder Alkenyl mit bis zu 6 Kohlenstoffen; oder Cycloalkyl mit bis zu 6 Kohlenstoffatomen oder Polyoxyalkylen mit bis zu 10 Kohlenstoffatomen; und R_8 mit der folgenden Formel:



wobei

$n = 3$ oder größer
 $p = 1$ bis 1000; und
 $q = 1$ bis 25.

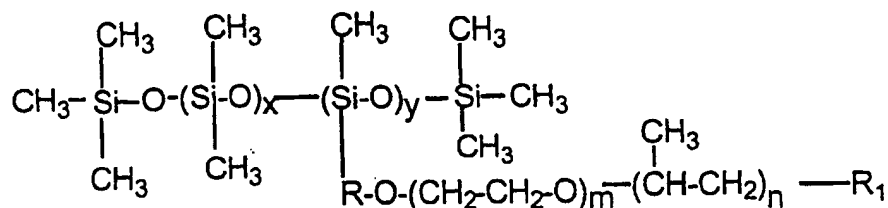
16. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) ein Silikon-Quarternär mit der folgenden Struktur ist:



wobei

$\text{R} =$ Alkylgruppe, $\text{C}_{12} - \text{C}_{18}$;
 $\text{Z} = -\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} - (\text{CH}_2)_3 -$;
 $\text{X} =$ Alkoxy, Chlorid oder anderes kompatibles Gegenion; und
 $n = 1$ bis 50.

17. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) ein Silikon-Quarternär mit der folgenden Struktur ist:



wobei

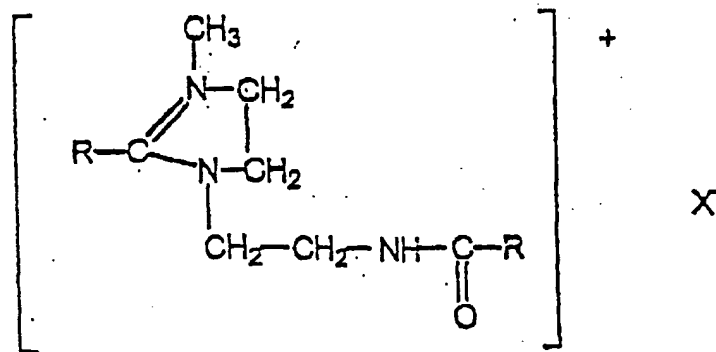
R = Alkylen, C₁ - C₈;
 R₁ = Acetat- oder Hydroxylgruppe;
 x = 1 bis 1000;
 y = 1 bis 50;
 m = 1 bis 30; und
 n = 1 bis 30.

18. Verfahren gemäß Anspruch 1, wobei wenigstens einer der Weichmacher/Bindungslöser in Schritt d) ein quarternisiertes, hydrolisiertes Weizenprotein / Dimethicon-Phosphocopolyol Copolymer ist.
19. Verfahren gemäß Anspruch 1, wobei der auf die getrocknete Bahn aufgebrauchte Weichmacher/Bindungslöser durch ein Lösungsmittel getragen wird, ausgewählt aus der Gruppe bestehend aus Wasser, Propylenglycol, Ethylenglycol, Polyethylenglycol, Isopropylalkohol, Methanol und Ethanol.

Revendications

1. Procédé de fabrication d'un papier absorbant mince et doux comprenant :

(a) la formation d'une suspension aqueuse de fibres papetières renfermant de 0,01 à 6 % en poids, par rapport aux fibres sèches, d'un composé ammonium quaternaire ayant la structure suivante :

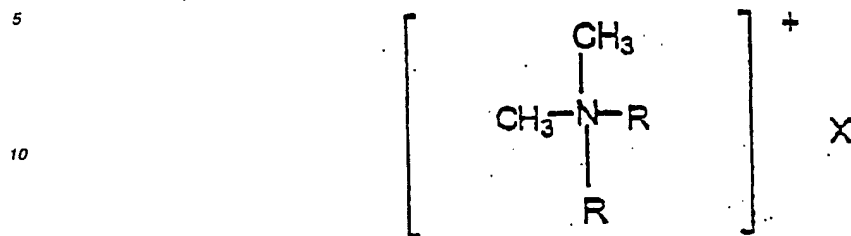


dans laquelle :

X = chlorure, méthylsulfate ou autre contre-ion compatible ; et
 R = aliphatique, saturé ou insaturé, en C₈-C₂₂ ;

- (b) la formation d'une nappe de papier absorbant mince par dépôt de la suspension aqueuse de fibres papetières sur une toile de formation ;
- (c) l'essorage et le séchage de la nappe de papier absorbant mince ; et
- (d) l'application locale à la nappe sèche de papier absorbant mince de 0,01 à 10 % en poids, par rapport aux fibres sèches, d'un ou plusieurs assouplissants/déliers choisis dans le groupe consistant en les composés ammonium quaternaire, les composés de protéines quaternisés, les phospholipides, les composés quaternaires de silicone, les polysiloxanes organoréactifs et les silicones glycols.
2. Procédé selon la revendication 1, dans lequel la quantité d'assouplissant/délier ajoutée à la suspension de fibres va d'environ 0,1 à 3 % en poids sec par rapport au poids des fibres.
3. Procédé selon la revendication 1, dans lequel la quantité d'assouplissant/délier appliquée localement à la nappe séchée va de 0,1 à 10 % en poids sec, par rapport à la quantité de fibres.

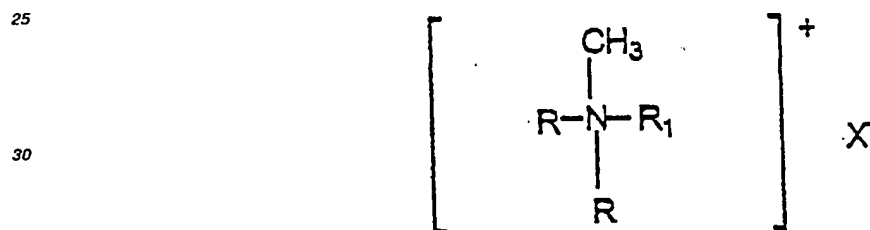
4. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé ammonium quaternaire ayant la structure suivante :



dans laquelle :

X = chlorure, méthylsulfate ou autre contre-ion compatible ; et
R = aliphatique, saturé ou insaturé, en C₈-C₂₂.

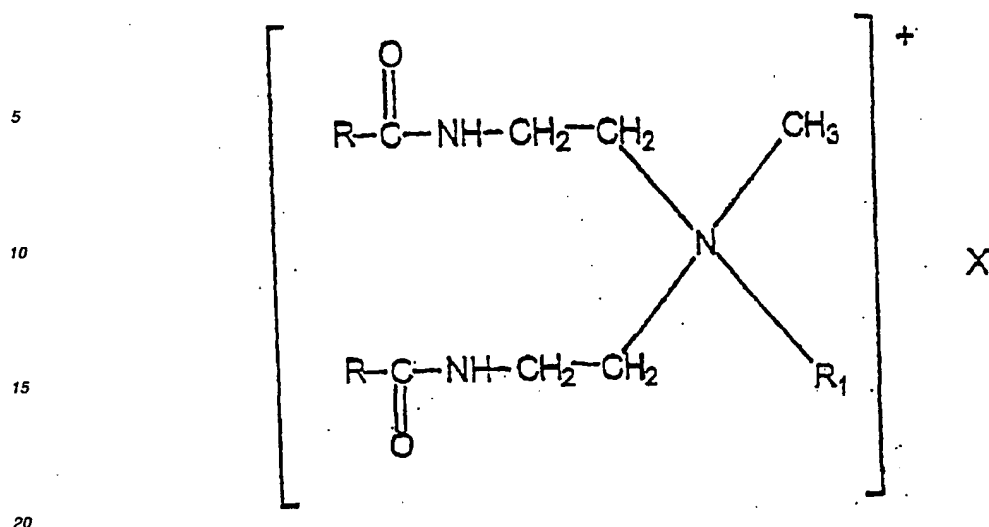
5. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé ammonium quaternaire ayant la structure suivante :



dans laquelle :

X = chlorure, méthylsulfate ou autre contre-ion compatible ;
R = aliphatique, saturé ou insaturé, en C₈-C₂₂ ; et
R₁ = groupe benzyle ou époxy.

6. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé ammonium quaternaire ayant la structure suivante :



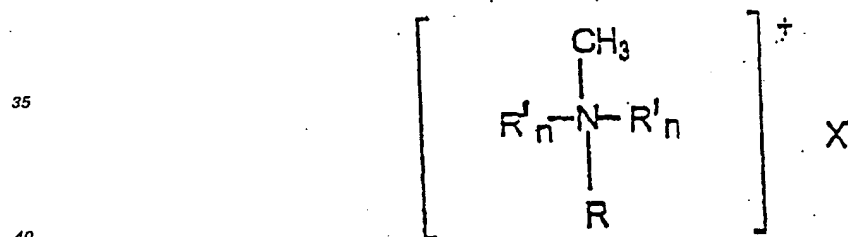
dans laquelle :

X = chlorure, méthylsulfate ou autre contre-ion compatible ;

R = aliphatique normal, saturé ou insaturé, en C₈-C₂₂ ; et

R₁ = 2-hydroxyéthyle ou 2-hydroxypropyle.

7. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé ammonium quaternaire ayant la structure suivante :



dans laquelle :

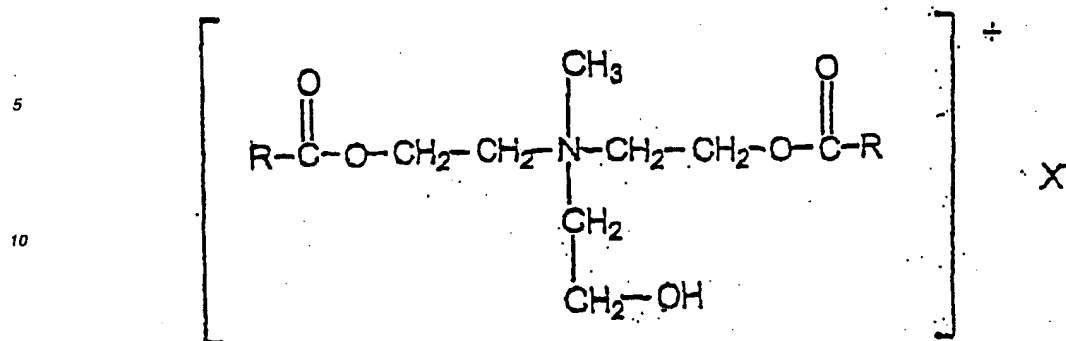
R = aliphatique, saturé ou insaturé, en C₈-C₂₂, normal ou ramifié ;

X = chlorure, méthylsulfate, éthylsulfate ou autre contre-ion compatible ;

R' = 2-hydroxyéthyle ou polyéthoxyéthanol ; et

n = 1 à 50.

8. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé ammonium quaternaire ayant la structure suivante :

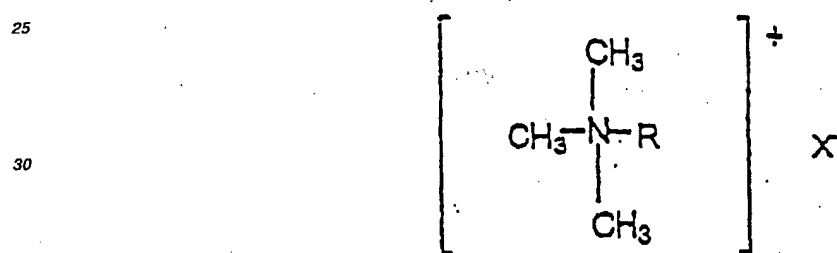


dans laquelle :

R = C₈-C₂₂ ; et

X = chlorure, méthylsulfate ou autre contre-ion compatible.

9. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé ammonium quaternaire ayant la structure suivante :

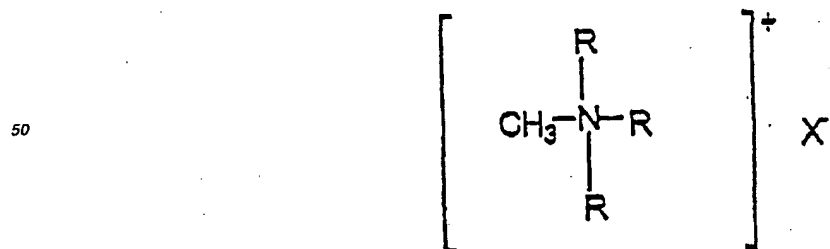


dans laquelle :

R = aliphatique, saturé ou insaturé, en C₈-C₂₂ ; ou allyle ; ou R'-O-CH₂-CH₂-CH₂ où R' = C₄-C₁₈ normal ou ramifié ; et

X = chlorure, sulfate ou autre contre-ion compatible.

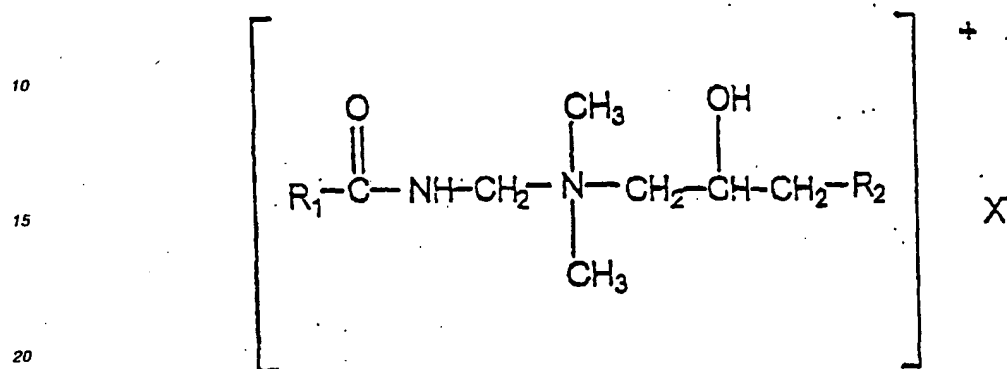
10. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé ammonium quaternaire ayant la structure suivante :



dans laquelle :

R = alkyle aliphatique, saturé ou insaturé, en C₈-C₂₂, normal ou ramifié ; et
 X = chlorure, méthylsulfate ou autre contre-ion compatible.

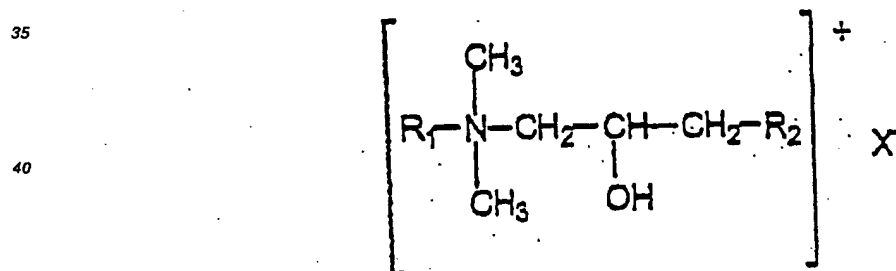
11. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé de protéine quaternisée ayant la structure suivante :



dans laquelle :

- R₁ = radical d'acide gras, saturé ou insaturé, en C₁₂-C₂₂ ;
 R₂ = protéine de soja hydrolysée, protéine de soie hydrolysée, protéine de farine hydrolysée, motif collagène, ou motif kératine ; et
 X = chlorure, lactate ou autre contre-ion compatible.

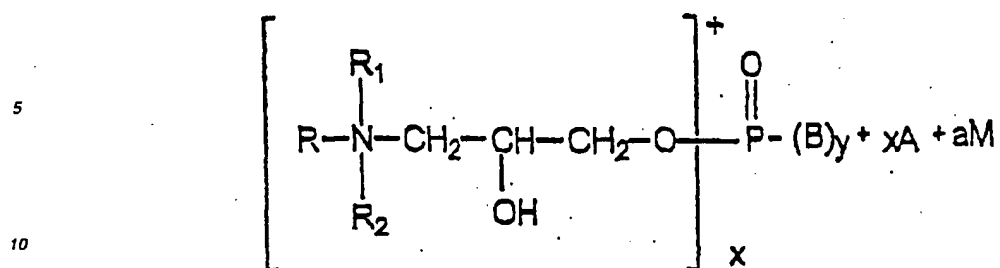
12. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un composé de protéine quaternisée ayant la structure suivante :



dans laquelle :

- R₁ = radical d'acide gras, saturé ou insaturé, en C₁₂-C₂₂ ;
 R₂ = collagène hydrolysé ou motif kératine ; et
 X = chlorure, lactate ou autre contre-ion compatible.

13. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un phospholipide ayant la structure suivante :



dans laquelle :

$x = 1 \text{ à } 3$;

$x + y = 3$;

$a = 0 \text{ à } 2$;

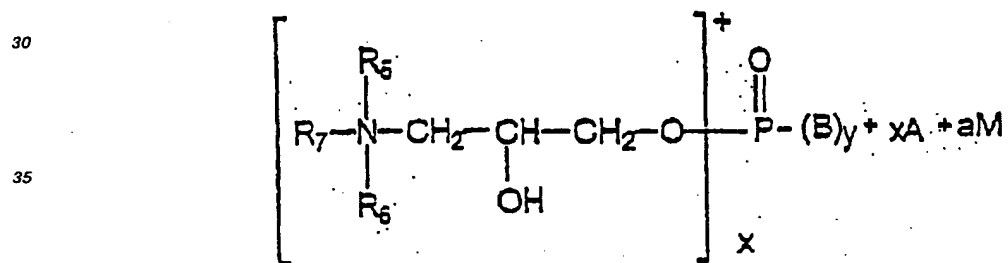
$B = O^-$ ou OM ;

$A = \text{un anion}$;

$M = \text{un cation}$; et

R, R_1 & R_2 qui peuvent être identiques ou différents, sont des groupes alkyle, alkyle substitué, alkylaryle ou alkényle ayant jusqu'au 16 atomes de carbone et le nombre total d'atomes de carbone de $R + R_1 + R_2 = 10 \text{ à } 24$.

14. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un phospholipide ayant la structure suivante :



dans laquelle :

$x = 1 \text{ à } 3$;

$x + y = 3$;

$a = 0 \text{ à } 2$;

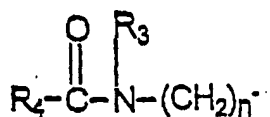
$B = O^-$ ou OM ;

$A = \text{un anion}$;

$M = \text{un cation}$; et

R_5 et R_6 , qui peuvent être identiques ou différents, représentent alkyle, hydroxyalkyle, carboxyalkyle allant jusqu'à C_6 , ou polyoxyalkylène allant jusqu'à C_{10} ; ou R_5, R_6 et l'atome d'azote auquel ils sont liés peuvent représenter un N-hétérocycle ; et

$R_7 = \text{motif amidoamine de structure :}$



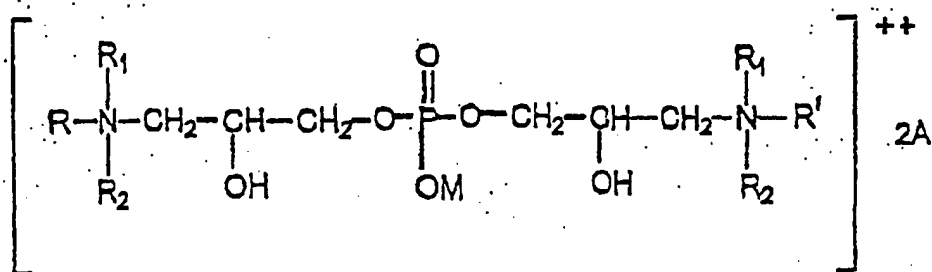
dans laquelle :

$n = 2 \text{ à } 6$;

$R_3 =$ hydrogène ou alkyle, hydroxyalkyle ou alkényle ayant jusqu'à 6 atomes de carbone ; ou cycloalkyle ayant jusqu'à 6 atomes de carbone, ou polyoxyalkylène ayant jusqu'à 10 atomes de carbone ; et

$R_4 =$ alkyle, alkényle, alkoxy ou hydroxyalkyle en C_5 - C_{21} , ou aryle ou alkaryle allant jusqu'à C_{20} .

15. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déliers de l'étape (d) est un phospholipide ayant la structure suivante :



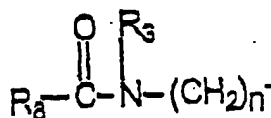
dans laquelle

A = un anion ;

M = un cation ;

R, R_1 & R_2 qui peuvent être identiques ou différents sont des groupes alkyle, alkyle substitué, alkylaryle ou alkényle ayant jusqu'à 16 atomes de carbone, et le nombre total d'atomes de carbone de $R + R_1 + R_2 = 10$ à 24 ; et

R' est un motif amidoamine de structure :

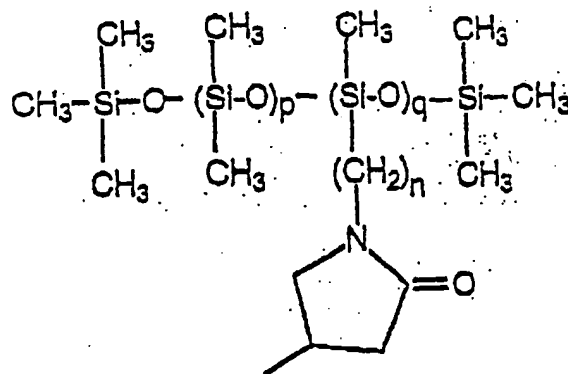


dans laquelle :

$n = 2 \text{ à } 6$;

$R_3 =$ hydrogène ou alkyle, hydroxyalkyle ou alkényle ayant jusqu'à 6 atomes de carbone ; ou cycloalkyle ayant jusqu'à 6 atomes de carbone ou polyoxyalkylène ayant jusqu'à 10 atomes de carbone ; et

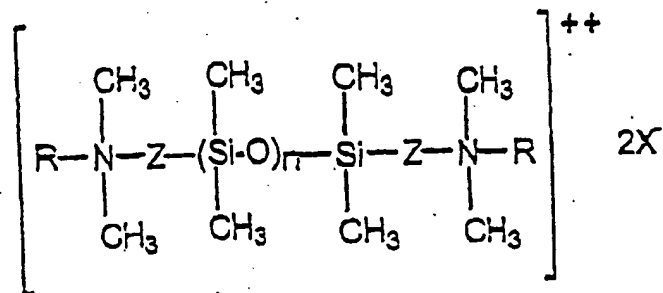
R_8 a la structure suivante :



dans laquelle :

$n = 3$ ou plus ;
 $p = 1$ à 1000 ; et
 $q = 1$ à 25 .

16. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déformants de l'étape (d) est un composé quaternaire de silicone ayant la structure suivante :



dans laquelle :

$\text{R} =$ groupe alkyle en C_{12} - C_{18} ;
 $\text{Z} = -\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-(\text{CH}_2)_3-$;
 $\text{X} =$ alkoxy, chlorure ou autre contre-ion compatible ; et
 $n = 1$ à 50 .

17. Procédé selon la revendication 1, dans lequel l'un au moins des assouplissants/déformants de l'étape (d) est un silicone ayant la structure suivante :



15

20

- 2.

3

3

4

•